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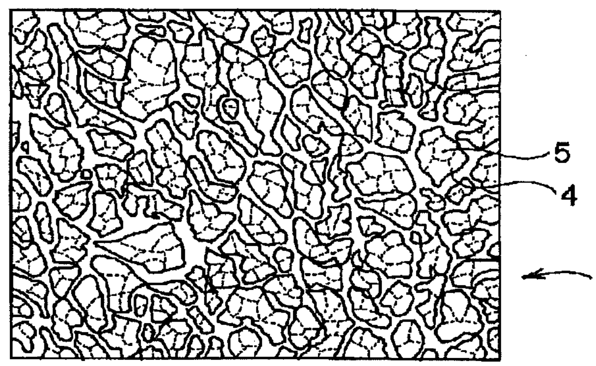
(54) [Title of the Invention] SURFACE TREATED ALUMINIUM MATERIAL AND MANUFACTURING METHOD THEREOF

(57) [Abstract]

[Problem] The present invention is to provide a surface treated aluminum material having an anodic oxide film structure which makes it possible to improve adhesion thereof to such a lamination resin material as a resin film, etc, and a manufacturing method thereof.



[Solving Means] The above-mentioned problem of a surface treated aluminum material 1 having an anodic oxide film 2 formed on the surface of aluminum or an aluminum alloy is solved by such a means that the anodic oxide film 2 is provided with a fine pore 5 inside a hole 4 of a porous layer 3. In this case, it is preferable that an open diameter W of the hole 4 of the porous layer 3 is 200～600 nm and an open diameter V of the fine pore 5 is 50～200 nm. Further, a manufacturing method of the surface treated aluminum material 1 according to the present invention is that of the surface treated aluminum having the above-mentioned structure, wherein the hole 4 of the porous layer 3 thereof is formed by the 1st anodizing treatment and the fine pore 5 is formed by the 2nd anodizing treatment.

[Claims]

[Claim 1] In a surface treated aluminum material having an anodic oxide film formed on the surface of aluminum or an aluminum alloy, an improvement being that the anodic oxide film has a fine pore inside a hole of a porous layer.

[Claim 2] The surface treated aluminum material according to claim 1, wherein an open diameter of the hole of the porous layer is 200～600 nm and an open diameter of the fine pore is 50～200 nm.

[Claim 3] In a manufacturing method of an anodic oxide film formed on the surface of aluminum or an aluminum alloy in which a fine pore is formed inside a hole of a porous layer of the anodic oxide film, an improvement being that the hole of the porous layer is formed by the 1st anodizing treatment and the fine pore is formed by the 2nd anodizing treatment at a voltage which is lower than a treating voltage applied in the 1st anodizing treatment.

[Detailed Description of the Invention]

[0001]

[Prior Art] The present invention relates to a surface treated aluminum material and a manufacturing method thereof, and, more in detail, relates to a surface treated aluminum material having an anodic oxide film making it possible to improve adhesion of such a lamination resin material as a resin film or the like thereto, and a manufacturing method thereof.

[0002]

[Description of Prior Art] Conventionally, there is a manner of using which uses a resin film as a laminate for an aluminum material. In this usage, a substrate treatment is beforehand applied to an aluminum material in general for improving adhesion of an aluminum material to a resin film. At this time, a phosphating chromate treatment or an anodizing treatment which can give unevenness or porous structure to the surface of the aluminum material is widely adopted as a substrate treatment. Further, as a method of laminating a resin film to an aluminum material, a thermal fusion is also adopted generally in order to bite the fused resin film into the unevenness or porous structure formed on the surface of the aluminum material and improve the adhesion.

[0003]

[Problem to be Solved by the Invention] However, since a treating solution used when the phosphating chromate treatment is carried out is harmful, such problems as a work environment, a waste liquid treatment, etc are raised.

[0004] Further, even in a case where the unevenness or porous structure is given to the surface of the aluminum material by the phosphating chromate treatment or anodizing treatment, the adhesion of the aluminum material to the resin film can not be improved sufficiently.

[0005] The present invention is to solve the above-mentioned problems, and provides a surface treated aluminum material having the structure of anodic oxide coating which makes it possible to improve the adhesion of lamination resin materials, such as a resin film or the like, and a manufacturing method thereof.

[0006]

[Means for Solving the Problem] The surface treated aluminum material according to claim 1 is that having an anodic oxide film which is formed on the surface of aluminum or an aluminum alloy, and is characterized in that the anodic oxide film has a fine pore inside a hole of a porous layer.

[0007] According to the present invention, since the anodic oxide film formed on the surface of aluminum or an aluminum alloy has the fine pore inside the hole of the porous layer, if a lamination

resin material such as a resin film is thermally fused, the fused lamination material is flowed and intruded into the fine pore made inside the hole of the porous layer and can exhibit an excellent anchor effect. The surface treated aluminum material having the anodic oxide film comprising such a characteristic structure can improve the adhesion to any of the lamination resin materials, such as a resin film or the like.

[0008] The present invention as recited in claim 2, in the surface treated aluminum material according to claim 1, it has such a characteristic feature that an open diameter of the hole of the porous layer is 200-600 nm, and an open diameter of the fine pore is 50～200 nm.

[0009] According to the present invention, the adhesion of the surface treated aluminum material to the such a lamination resin materials as a resin film or the like can be improved by limiting the open diameter of the hole of the porous layer and the open diameter of the fine pore to the above-mentioned respective ranges and an excellent anchor effect can be brought about by intrusion of the flow resin therein.

[0010] A manufacturing method of the surface treated aluminum material as recited in claim 3 is such that, in a manufacturing method of forming an anodic oxide film on the surface of aluminum or an aluminum alloy in which the fine pore is formed inside the hole of the porous layer of the anodic oxide film, an improvement being that hole of the porous layer is formed by the 1st anodizing treatment and the fine pore is formed by the 2nd anodizing treatment at a voltage which is lower than a treating voltage applied in the 1st anodizing treatment.

[0011] According to the present invention, since the hole of the porous layer is formed by the 1st anodizing treatment and the fine pore is formed by the 2nd anodizing treatment applied with a voltage which is lower than that applied in the 1st anodizing treatment, a surface treated aluminum material having the fine pore can be made inside the hole of the porous layer of the anodic oxide film without using a harmful treating solution, and at the same time, since the hole of porous layer and the fine pore which secure the adhesion between the resin material and the surface treated aluminum material can be made, a surface treated aluminum material which is excellent in adhesion of any of the lamination resin materials such as a resin film or the like to be applied thereafter to the surface treated aluminum material can be manufactured.

[0012]

[Mode of Embodiment of the Invention] A surface treated aluminum material and a manufacturing method thereof according to the present invention will be explained with reference to the drawings. FIG. 1 is an enlarged and schematic plan view showing one example of the surface

treated aluminum material according to the present invention. FIG. 2 is an expanded and schematic sectional view of FIG. 1.

[0013] As shown in FIG. 1 and FIG. 2, a surface treated aluminum material 1 of the present invention is an aluminum material comprising an anodic oxide film 2 formed on the surface of aluminum or an aluminum alloy, and the characteristic feature thereof is that the formed anodic oxide film 2 has fine pores 5 inside each of holes 4 of a porous layer 3.

[0014] Since the surface treated aluminum material 1 having such a feature has the structure which consists of the holes 4 which constitute the porous layer 3 and the fine pores 5 made inside the holes 4, when the such a lamination resin material as a resin film or the like is thermally fused, for example, the fused laminating material is flowed and intruded into the hole 4 of the porous layer 3 and the fine pores 5 made inside the holes and an excellent anchor effect can be exhibited. As a result, the surface treated aluminum material 1 having such an anodic oxide film 2 brings about such an exceptional effect that the adhesion of the lamination resin materials, such as a resin film to the surface treated aluminum material 1 can be remarkably improved.

[0015] As an applicable aluminum material, there is no limitation especially, and a common aluminum material or aluminum alloy material which is capable of forming the anodic oxide film 2 can be applied preferably. Above all, the aluminum material which can be used by thermally fusing any kind of lamination resin materials, such as a resin film, etc. is preferable.

[0016] The anodic oxide film 2 has a barrier layer 9 and the porous layer 3 like a common anodic oxide film. The thickness t of the anodic oxide film 2 is preferably 30～400 nm, and more preferably is 100～300 nm. The reason for limiting the thickness t of the anodic oxide film 2 to such a range is that if the thickness t is less than 30 nm, it becomes difficult to form such a characteristic structure according to the present invention which will be explained later, and that if the thickness t exceeds 400 nm, it becomes easy to produce cracks in the anodic oxide film itself. Further, the thickness t here is represented by the average value of the values measured with an EPMA.

[0017] The porous layer 3 is the porous layer formed simultaneously with the barrier layer 9 formed by the anodizing treatment, and means a portion at which the holes 4 having a depth D are made. As for the depth D (namely, the thickness of the porous layer 3) of the holes 4, in the present invention, it is preferable that the depth D is 60～100 nm. This depth D corresponds to the thickness t of the anodic oxide film 2 as mentioned above, and if the thickness t of the above-mentioned anodic oxide film 2 is thin, the depth D of the holes 4 also naturally becomes

small, and if the thickness t of the above-mentioned anodic oxide film 2 is thick, depth D of the holes 4 becomes large. The depth D here is represented by the average value of the values measured with Nanoscope IIIa of AFM Biko Co. make.

[0018] According to the present invention, an open diameter W of the holes 4 is preferably 200 nm ~600 nm, and more preferably 350~500 nm. By limiting the open diameter W of the holes 4 to such a range and also on the basis of the action of fine pores 5 fmade inside the holes 4, an excellent anchor can be exhibited between the such a lamination material as a resin film or the like and the surface treated aluminum material. If the open diameter W of the holes 4 is less than 200 nm, a laminating synthetic resin material such a resin film, or the like fluidizing at the time of thermal adhesion is difficult to flow into the holes 4 and the fine pores 5 made inside the holes and, as a result, it becomes difficult to exhibit a sufficient anchor effect, and if the open diameter W exceeds 600 nm, the laminating synthetic resin material flowing at the time of thermal fusion flows easily into the holes 4 and the fine pores 5 made inside the holes, but the laminating resin material after solidification thereof becomes easy to detach from the holes 4 and it happens that it becomes difficult to exhibit the sufficient anchor effect. Further, the open diameter W of the holes 4 is represented by the average value of the values enlarged and measured with Nanoscope IIIa of AFM Biko Co. make.

[0019] The fine pores 5 are the characteristic portion of the present invention, and are made in inside the holes 4 of the porous layer 3. More in detail, it is preferable to form the pores 5 having such a size that the open diameter V is 50~200 nm, preferably 100~150 nm and the depth d is 10~50 nm at the bottom 4a or the side surface 4b of each of the holes 4 having the depth D and the open diameter W as mentioned above. The number of the fine pores 5 to be made is not limited especially, but it is preferable that a large number of the fine pores 5 are made at the bottom 4a or the side surface 4b of the hole 4.

[0020] By limiting the open diameter V and depth d of fine pores 5 to such respective ranges, and on the basis of an action of the fine pores 5, an excellent anchor effect can be exhibited between the flowing lamination resin material such a resin film or the like and the surfaces treated aluminum material. If the open diameter V is less than 50 nm, such a flowing lamination synthetic resin material as a resin film or the like at the time of thermal fusion is difficult to flow into the fine pores 5 and intruded therein, and as a result, it becomes difficult to exhibit a sufficient anchor effect, and if the open diameter V exceeds 200 nm, the lamination synthetic resin material fluidizing at the time of thermal adhesion flows easily into the fine pores 5, but the lamination

resin material after solidification thereof becomes easy to be detached from the fine pores 5 and it happens that it becomes difficult to exhibit the sufficient anchor effect. The depth d of the fine pores 5 has relations with the thickness of the bottom 4a or the side surface 4b of the holes 4 constituting the porous layer 3, and a preferable anchor effect can be exhibited by the depth d in the foregoing range. Further, the open width V here is represented by the average value of the values enlarged and measured with an electron microscope, and also the depth d here is represented by the average value of the values measured with Nanoscope IIIa of AFM Biko Co. make.

[0021] With the surface treated aluminum material 1 comprising such a structure as above according to the present invention, when such a lamination resin material as a resin film or the like is laminated and adhered thereto by the thermal fusion or the like as mentioned above, the lamination resin material which is fluidized at the time of the thermal fusion treatment is flowed into the holes 4 and the fine pores 5 and intruded therein, so that an excellent anchor effect can be exhibited between the fused lamination resin material and the surface treated aluminum material. Further, as for lamination resin materials to be laminated to the surface treated aluminum material, as long as the materials can exhibited between the same and the surface of the surface treated resin material 1, they are suitable. Resin films which are capable being fused by heat, or coating films comprising organic materials or the like are suitably used.

[0022] Next, a manufacturing method of the surface treated aluminum material according to the present invention is explained as follows.

[0023] A manufacturing method of the surface treated aluminum material 1 of this invention, is characterized in that for manufacturing the surface treated aluminum material 1 having fine pores 5 in the inside of each of the holes 4 of the porous layer 3 of the anodic oxide film 2, the holes 4 of the porous layer 3 are made by the 1st anodizing treatment, and the fine pores 5 are made by the 2nd anodizing treatment.

[0024] The anodic oxide film 2 of the present invention can be obtained by adopting the principle of a general anodizing treatment method as it is. If one example is given, after a predetermined aluminum material is degreased and washed, an electrolytic polishing is performed, and after washed, an anodizing treatment is carried out in an electric cell. In such steps, it is possible to add any other pretreatment step or after-treatment step, if necessary.

[0025] As for electrolytes, a phosphoric acid solution, a sulfuric acid solution, a sulfamic acid solution, an oxalic acid solution, etc. can be used. The anodizing treatment is performed in such a

manner that an aluminum material is used as the anode and an electrolytic treatment is carried out in an electrolyte of 20～40 ℃. According to the present invention, the electrolytic treatment is carried out at two steps of the 1st anodizing treatment and the 2nd anodizing treatment.

[0026] The 1st anodizing treatment is carried out by using the pretreated aluminum material as the anode and applying a voltage V1 of about 10～30V thereto. By the 1st anodizing treatment, the barrier layer 9 and the porous layer 3 which comprise the predetermined sized holes 4 are formed. The open diameter W and the depth D of the holes 4 as mentioned above are adjusted by mainly setting the condition of the voltage arbitrarily.

[0027] The 2nd anodizing treatment is carried out for the purpose of forming the fine pores 5 inside the holes 4 formed by the 1st anodizing treatment as mentioned above, and is performed by using the aluminum material already treated by the 1st anodizing treatment as the anode, and applying the voltage V2 of about 5～20V thereto. In this case, it is necessary that the voltage V2 applied at that time is lower than the voltage V1 applied at the time of the 1st anodizing treatment. The diameter V and the depth d of the fine pores 5 as mentioned above are adjusted by mainly setting the condition of voltage, arbitrarily.

[0028] According to the manufacturing method of the surface treated aluminum material 1 as mentioned above, the holes 4 of the porous layer 3 are formed by the 1st anodizing treatment, and the fine pores 5 are formed by the 2nd anodizing treatment applied with the voltage lower than the voltage applied by the 1st anodizing treatment, so that a lot of the fine pores 5 can be formed inside the holes 4 of the porous layer 3 of the anodic oxide film 2. Owing to the holes 4 of the formed porous layer 3 and the fine pores 5 which are formed by this way, the adhesion of such a lamination resin material as a resin film laminated thereafter to the holes and fine pores can be improved and there can be obtained the surface treated aluminum material 1 which is excellent in adhesion.

[0029]

[Examples] The present invention is explained more in detail by examples and comparative examples as follows.

[0030] (Examples 1～10) A 0.3 mm-thick 5052 material was used as an aluminum material. The aluminum material was pretreated in order of degreasing, washing, de-smutting and rinsing, and the aluminum material was then immersed into a 10% phosphoric acid solution set at a temperature of 30 ℃, and an anodizing treatment thereof was carried out. The anodizing treatment was carried out by using the aluminum material as the anode and an electrolysis

treatment was carried out for respective test samples by applying the direct current voltages as shown in Table 1. In the first place, the 1st anodizing treatment for the respective test samples was carried out at the predetermined voltages V1 as shown in Table 1, for 10 seconds, and the 2nd anodizing treatment was carried out at the predetermined voltages V2 as shown in Table 1, for 10 seconds. The total electrolytic time was 20 seconds. As a result, the holes 4 were formed by the 1st anodizing treatment and the fine pores 5 were formed inside the holes 4 by the 2nd anodizing treatment. Further, the thickness t of the formed anodic oxide films 2 for each test example is the average value of the values measured by EPMA (form: JXA-8900RL, JEOL Co., Ltd. make).

The open diameter W of the holes 4 and the diameter V of the fine pores 5 for each of the test examples are the average value of the values enlarged by 100,000 times and measured with the electron microscope (form :JAMP-7800F, JEOL Co., Ltd. make).

In this way, the surface treated aluminum materials 1 of examples 1～10 of the present invention were obtained.

[0031] (Comparative examples 1 and 2) As shown in Table 1, the surface treated aluminum materials of comparative examples 1 and 2 were obtained by making the voltage V2 applied in the 2nd anodizing treatment higher than the voltage V1 applied in the 1st anodizing treatment.

[0032] (Comparative example 3) The surface treated aluminum material of a comparative example 3 was obtained without the 2nd anodizing treatment except for that the anodizing treatment was carried out under the same condition as that carried out in the above-mentioned examples.

[0033] (Comparative example 4) The surface treated aluminum material of a comparative example 4 was obtained by giving the chromate treatment to the above-mentioned aluminum material.

[0034] (Evaluation of adhesion) A 15 μm -thick polyester film used as the resin film 6 was fused by heat to the surface of each of the test samples obtained by examples 1～10 and comparative examples 1～4. The thermally fusion temperature was about 200 ℃. The lamination material 10 thus obtained was immersed in hot water of 50 ℃ for 30 minutes. After immersion, the lamination material 10 was slitted in the surface thereof and was folded. The form of a test sample 7 at this time is shown in FIG. 3. And the folded parts of the lamination material 10 were fixed respectively to chucks 11 and 12 of a tension tester. The evaluation of adhesion of each test sample was made by a peeled length of the resin film 6 when the resin film 6 was pulled at a pull speed of 5mm/min by the tension tester.

[0035] The adhesion of each of the test samples was evaluated in such a manner that these

which were not peeled at all and were torn to pieces were represented by a symbol ◎, these which were torn to pieces at the peeled length of not less than 1 mm were represented by a symbol ○, these which were torn to pieces at the peeled length between from more than 1 mm to less than 5 mm were represented by a symbol △ and these which were torn to pieces at the peeled length of more than 5 mm were represented by a symbol ×. The results thereof are shown in Table 1.

[0036]

[Table 1]

	V1 (V)	V2 (V)	Film thickness t (nm)	Open diameter W (nm)	Open diameter V (nm)	Adhesion
Example 1	15	10	150	400	120	◎
Example 2	12	8	100	350	100	◎
Example 3	30	15	300	450	140	◎
Example 4	35	30	400	550	100	○
Example 5	15	10	30	200	50	○
Example 6	20	10	200	220	180	○
Example 7	35	20	350	400	200	○
Example 8	10	5	70	220	100	○
Example 9	15	5	30	150	50	△
Example 10	35	30	400	600	220	△
Comparative example 1	10	15	150	400	20	×
Comparative example 2	5	15	25	100	10	×
Comparative example 3	15	–	200	300	–	×
Comparative example 4	Chromate treatment					×

[0037]

[Effect of the Invention] As explained above, since the surface treated aluminum material according to the present invention is such that the fine pores are formed inside the holes of the porous layer of the anodic oxide film, if such a lamination resin material as a resin film or the like is thermally fused to the aluminum material of which the surface has such an anodic oxide film, the lamination resin material is fluidized and intruded in the fine pores made inside the holes of the porous layer, so that an excellent anchor effect can be exhibited. Thus, the surface treated aluminum material having the anodic oxide film comprising such a characteristic structure can improve the adhesion to such a lamination resin material as a resin film, etc.

[0038] Further, according to the manufacturing method of the surface treated aluminum material

according to the present invention, the holes of the porous layer are formed by the 1st anodizing treatment and the fine pores are formed by the 2nd anodizing treatment, so that the surface treated aluminum material having the fine pores made inside of the holes of the porous layer of the anodic oxide film can be manufactured without using a harmful treating solution and also the surface treated aluminum material which is excellent in adhesion to such lamination resin material as a resin film, etc. to be laminated thereto later can be manufactured.

[Brief Description of the Drawings]

[FIG. 1] is a schematic and enlarged plan view showing one example of the surface treated aluminum material according to the present invention.

[FIG. 2] is an enlarged sectional view of FIG. 1.

[FIG. 3] is a schematic sectional view showing one example of a test mode at the time of adhesion evaluation.

[Description of Symbols]

1 Surface treated aluminum material

2 Anodic oxide film

3 Porous layer

4 Hole

4a Bottom

4b Side surface

5 Fine pore

6 Resin film

7 Test sample

9 Barrier layer

10 Lamination material

11, 12 Chuck

t Film thickness of an anodic oxide film

W Open diameter of the hole

V Open diameter of the fine pore

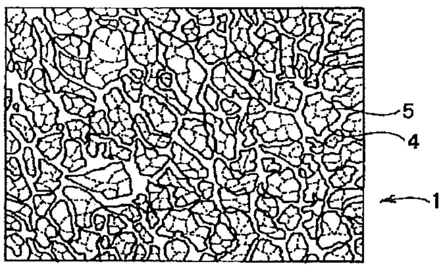
D Depth of the hole

d Depth of the fine pore

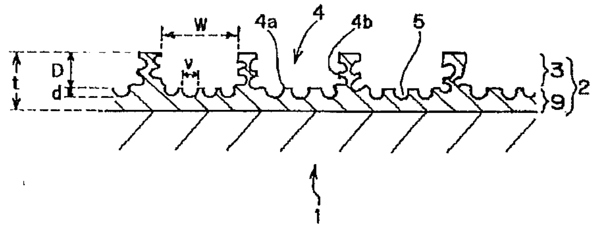
V1 Treating voltage applied in the 1st anodizing treatment

V2 Treating voltage applied in the 2nd anodizing treatment

[FIG.1]



[FIG.2]



[FIG.3]